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# Photo-Switching Based on Azobenzene Functionalized Graphene

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**ABSTRACT:** An enhanced photoinduced reversible switching of graphene oxide-azobenzene (GO-AZO) hybrid was investigated as a highly sensitive photo-switch. The internal short-range ordered crystalline structure of GO-AZO hybrid was advantageous to charge transfer. The AZO moieties on GO underwent a rapid *trans-cis* photoisomerization upon ultraviolet irradiation due to the electron interaction between AZO and GO. The GO-AZO hybrid film showed an enhanced reversible photo-switching performance with high on/off ratio of 8 and fast response time less than 500 ms.

## Introduction

Photocurrent generation based on a single molecule or hybrid building blocks offers a significant potential to photoconversion devices such as phototransistors,[1] photodetectors[2] and optical telecommunications.[3] The photochromic materials which can isomerize uniformly under the irradiation have been regarded as promising vital candidates for light-driven switching devices.[4] Among several complicated examples, azobenzene molecules with *trans-cis* conformations are widely studied as a pivotal switchable core due to high sensitivity and reversibility.[5, 6] With good thermal stability and detectability, the azobenzene is capable of a fast, efficient and fully reversible isomerization essential for the photocurrent switching functionalities. Although current studies were focused on polymers with azobenzene moieties due to good stability and reversibility,[7] the architecture of the azo-based photo-switching nano-materials is far from the deep understanding or precise control in terms of charge generation and transport. One of important paths to facilitate charge generation, separation, and transport is the synthesis of unique azobenzene nano-hybrids with electron donor-acceptor units. Excitingly, the efficient charge transfer between azobenzene moieties and carbon nanotubes (CNTs) or graphene enables the effective and reversible photoisomerization due to the enhanced quantum yield.[8, 9] However, the outstanding switch performance of the devices highly depends on the structures and properties of nano-hybrids. It has been proved that both CNTs and graphene exhibit remarkable optical and electronic properties that qualify them for applications in optoelectronic devices.[10-12] Photo-switches based on azobenzene functionalized CNTs have been realized with the outstanding switch performance due to efficient charge transfer, showing a fast increase of drain current within several seconds.[13] Compared with CNTs, graphene, a new unique member of carbon nano-materials, offers a perfect channel favoring

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carrier mobility and ballistic transport due to its two-dimensional hexagonal lattice structure.[14, 15] Thus the incorporation of azobenzene chromophore into the graphene sheets promisingly leads to vital advances in photocurrent switching because of the functional synergy. In this paper, graphene oxide (GO) covalently functionalized by an azobenzene molecule, 2-aminoazotoluene (AZO), was synthesized and characterized. The *trans-cis* isomerization of the AZO moieties on GO irradiated by monochromatic ultraviolet (UV) light was investigated by the ultraviolet-visible (UV-Vis) spectra. The GO-AZO hybrid film showed a rapid and reversible on/off photocurrent switching behavior by the alternative UV irradiation.

**Experimental Section**

**Materials.** GO was produced by the modification of Hummers method through the acid oxidation of flake graphite.[16, 17] The AZO was purchased from Tokyo Chemical Industry without any treatment.

**Preparation of the GO-AZO hybrid.** The synthesis of the GO-AZO hybrid was carried out through an amide linkage.

**Characterizations.** Transmission electron microscopy (TEM) analysis was performed on a Phlilps Tecnai $G^2$ F20 electron microscope at 200 kV. The UV-Vis absorption and fluorescence spectra were recorded in DMF solution on a Hitachi 330 UV-Vis spectrophotometer and a Hitachi F4600 fluorescence spectrophotometer, respectively. Time evolution of the absorption spectra of the GO-AZO hybrid in DMF upon irradiation of UV light at 365 nm was performed by a UV-GUN (2.45 mW/cm$^2$, ELC-403, ELECTRO- LITE CORPORATION). *I-V* characteristic of the GO-AZO hybrid film was investigated at room temperature using a Keithley 2635 instrument. The measurement of photo electrical response was performed on a PARSTAT 2273 advanced electrochemical system.

**Results and Discussion**

The morphologies of GO and GO-AZO were observed by TEM shown in figure 1. Figure 1(a) is a typical TEM image of GO, showing that individual GO sheets resemble crumpled silk veil waves in low-magnification image. After a long reaction time, the GO sheets become fluffy due to organic linkage of AZO and the re-aggregation of smaller flakes (figure 1(b)). A lattice resolved high resolution TEM image of the stacked GO-AZO lattice is shown in figure 1(c). An internal short-range ordered crystalline structure is observed. The average inter-planar distance was measured to be (0.35 ± 0.02) nm. The XRD patterns of GO and GO-AZO in figure 1(d) confirm that the chemical modification has a strong impact on the domain structure of the GO lattice. The characteristic 2θ peak of GO appearing at 12.1° corresponds to the (0 0 1) inter-planar spacing of 0.73 nm caused by the oxygen-rich groups on both sides of the sheets and water molecules trapped between the sheets.[18] In the case of GO-AZO, the intense (0 0 1) peak almost disappears while two broad diffraction peaks appear at 2θ = 25.3° and 42.5°, corresponding to the d-spacing of 0.35 and 0.21 nm, respectively, which are more likely to be the (0 0 2) and (1 0 0) peaks of graphite.[19] This result is consistent with the TEM observation. After the covalent functionalization, the electrostatic repulsion balance existed among the GO lattices is disturbed, the GO sheets tend to aggregated due to the strong van der Waals force, thus showing an internal short-range ordered structure.[18]

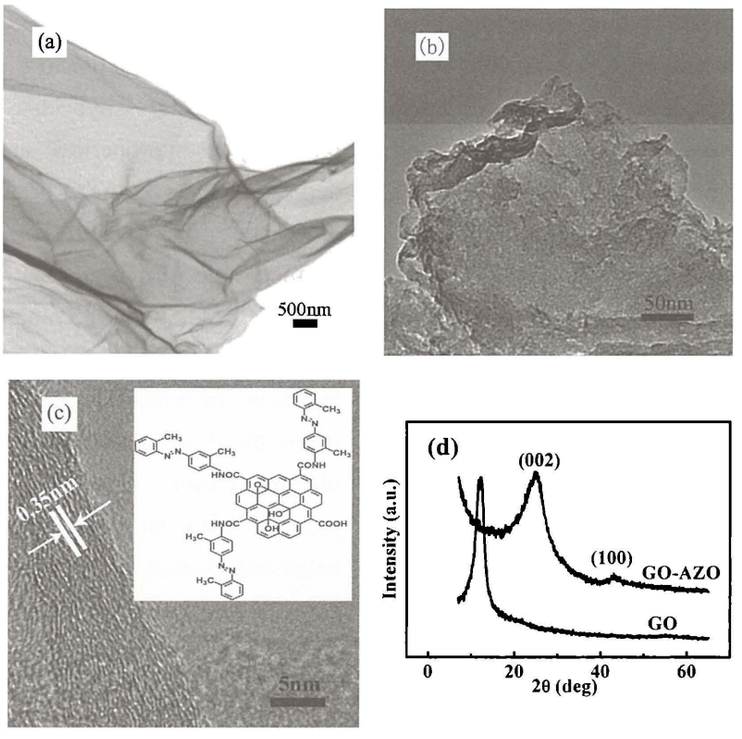


**Figure 1** Representative low-magnification TEM images of (a) GO and (b) GO-AZO. (c) Lattice resolved high resolution TEM image of the stacked GO-AZO nanosheets. Inset shows the chemical structure of GO-AZO. (d) XRD patterns of GO and GO-AZO.

The absorption and fluorescence (excitation at 480 nm) spectra of GO-AZO and the pristine AZO are shown in figure 2. The AZO (figure 2(a)) has an absorption maximum at 402 nm due to the $\pi$-$\pi^*$ transition of the *trans* AZO units. For GO-AZO, a new absorption peak centered at 320 nm and the hyperchromicity over the entire range (270-650 nm) are observed due to the introduction of the GO sheets. The GO-AZO in figure 2(d) shows a dramatic fluorescence quenching compared with AZO due to the photoinduced electron or energy transfer from the AZO chromophore to the GO sheets.[19, 20] The spectral measurements testify the strong electronic interactions between the AZO and the GO sheets.

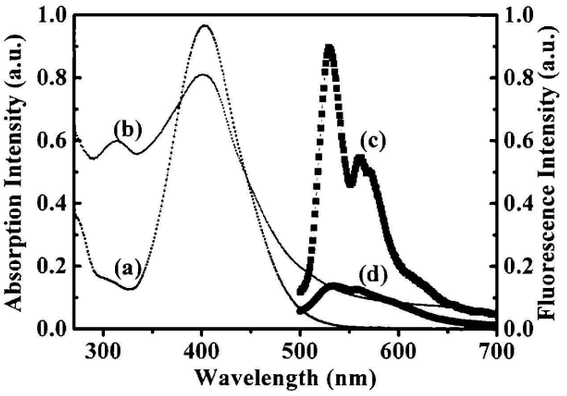


**Figure 2** Absorption spectra of (a) AZO and (b) GO-AZO as well as the corresponding fluorescence spectra of (c) AZO and (d) GO-AZO in DMF. Excitation wavelength is 480 nm.

Previous studies revealed that the photoisomerization of an azobenzene molecule could be tracked by the evolved absorption

intensity.[21] Figure 3 shows time evolution of the absorption spectra of AZO and GO-AZO irradiated by UV light at 365 nm. Both AZO and GO-AZO show continuous decreases in the band of the *trans* AZO units due to the *trans-to-cis* transition until a photostationary equilibrium is established. The isosbestic point of GO-AZO at 354 nm blue-shifted by 12 nm compared with that of AZO is attributed to the isomerization on GO sheets via covalent bonding. The efficient and fast conformation changes of azobenzene moieties on GO sheet offer a great potential to advanced light-modulated active materials for photo-switch.

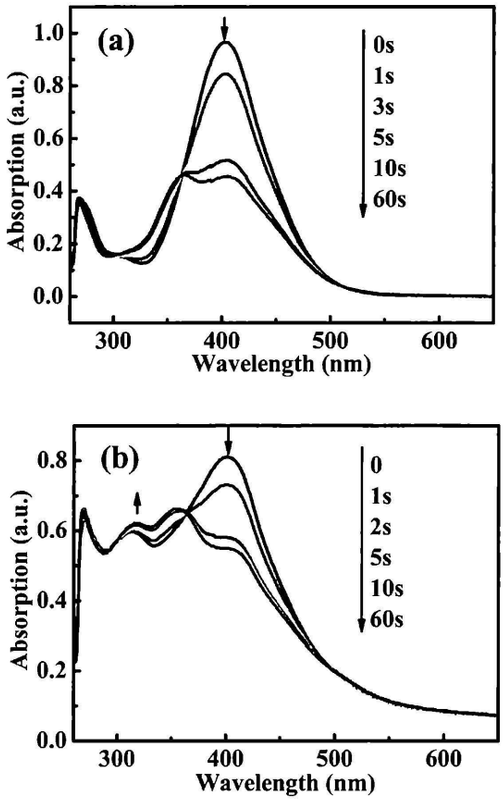


**Figure 3** Changes in the absorption spectra of (a) AZO and (b) GO-AZO in DMF upon irradiation at 365 nm. Arrows indicate the changes upon irradiation.

Efficient electron or energy transfer from the AZO to GO is essential to the photoresponse of the GO-AZO hybrid. Therefore, the photoresponse properties are investigated by depositing the GO–AZO or AZO DMF solution onto the ITO electrode. The typical *I-V* characteristics of the pristine AZO and GO-AZO with UV irradiation (365 nm, 2.45 mW/cm$^2$) or in dark are shown in figure 4. As shown, the photocurrent is drastically increased for GO-AZO when the UV irradiation is on. However, no obvious current increase is observed for the pristine AZO, which clearly confirms that the enhanced photoresponse of the GO-AZO hybrid is due to the synergy of the AZO and GO.

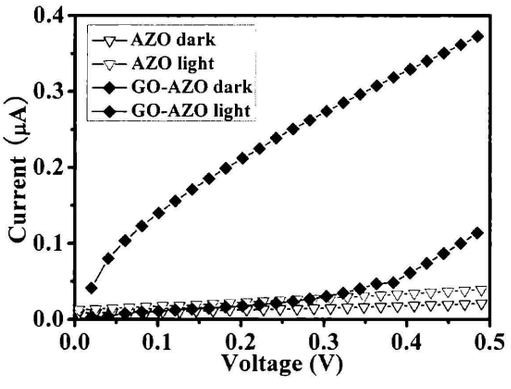


**Figure 4** Typical *I-V* characteristic of the pristine AZO and GO-AZO with and without UV irradiation (365 nm, 2.45 mW/cm$^2$).

The photocurrent switching performances were studied on an advanced electrochemical system using a three-electrode configuration. As shown in figure 5A, the GO-AZO hybrid shows the function of photocurrent switchers when the UV light is switched on and off. When 365 nm UV light is applied, a fast response of increased current can be found in the GO-AZO film and this change is reversible after the light is turned off while smaller response current is observed for

AZO under the same conditions. For GO-AZO, the ratio of the photocurrent under the UV irradiation to that under the dark (on/off ratio) is about 800%, which is much larger than that of recent reports.[13] It is also worth mentioning that the photoresponse time of the GO-AZO hybrid can be lower than 500 ms (figure 5B), while the pristine AZO failed to arrive at the saturation zone. This photoresponse is faster than that of other similar carbon-based donor-acceptor systems.[22-23] The dramatic enhancement in the photocurrent and the shorter photoresponse time indicate that the robust combination and good interfacial contact built between the AZO moieties and the GO sheets facilitate photoinduced carrier transfer. The AZO chromophore with molecular backbone undergoing a fast isomerization transition is available for high electron mobility.[24] Therefore, in the GO-AZO hybrid, the AZO moieties with high carrier mobility act as the electron donor and the flat GO sheets are good electron acceptor. Under UV irradiation, photoinduced electrons are scavenged by the GO nanosheets and percolate to the collecting electrodes, giving rise to large photocurrent. After turning off the light, the current decreased immediately for the recombination of close electrons and holes. A fast electron transport from the AZO to GO can be occurred within this intramolecular donor-acceptor system. This fast and efficient photocurrent response property facilitates its usage in photocurrent conversion devices modulated by UV light.

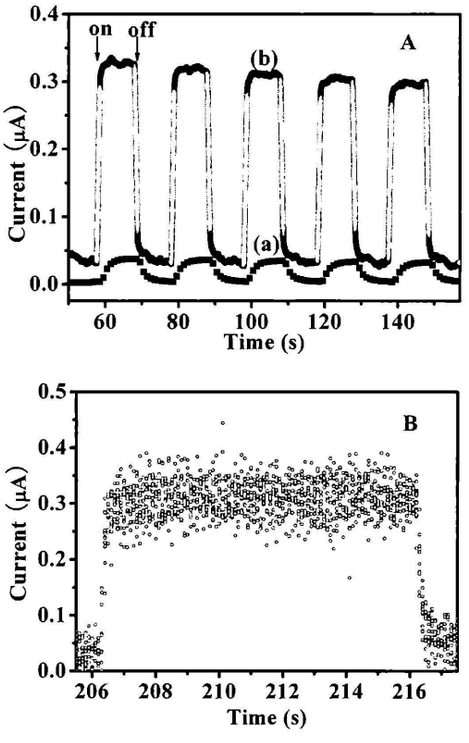


**Figure 5** (A) Photocurrent response of (a) the pristine AZO and (b) GO-AZO film at a +0.5 V bias in 0.1 M KCl aqueous solution. (B) Photocurrent response of GO-AZO in one on/off cycle.

## Conclusions

GO-AZO hybrid was synthesized by a covalent bond of AZO onto the GO sheets. The AZO moieties bonding on GO underwent a fast *trans-cis* photoisomerization facilitated by the high electron mobility within the molecular backbone. The photocurrent response of the GO-AZO film showed a rapid and reversible response of photocurrent upon UV irradiation, implying an efficient charge transfer from the AZO moieties to GO within the hybrid donor-acceptor system. The highly sensitive photoresponse properties make the GO-AZO hybrid a potential candidate for photocurrent switching applications.

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